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THE PREPARATION OF SILICON-CONTAINING CERAMICS BY
ORGANOSILICON POLYMER PYROLYSIS

by

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INTRODUCTION AND GENERAL COMMENTS

Silicon-containing ceramics include the oxide materials, silica and silicates; the binary compounds of silicon with non-metals, principally silicon carbide and silicon nitride; silicon oxynitride and the sialons; main group and transition metal silicides, and, finally, elemental silicon itself. There is a vigorous research activity throughout the world on the preparation of all of these classes of solid silicon compounds by the newer preparative techniques.

Silicon carbide SiC [1] and silicon nitride Si_3N_4 [2], have been known for some time. Their properties, especially their high thermal and chemical stability, their hardness, their high strength, as well as other properties have led to useful applications for both of these materials. The "conventional" methods for the preparation of SiC and Si_3N_4 , the high temperature reaction of fine grade sand and coke (with additions of sawdust and NaCl) in an electric furnace (the Acheson process) for the former and usually the direct nitridation of elemental silicon or the reaction of silicon tetrachloride with ammonia (in the gas phase or in solution) for the latter, do not involve soluble or fusible intermediates. For many applications of these materials this is not necessarily a disadvantage (e.g., for the application of SiC as an abrasive), but for some of the more recent desired applications soluble or fusible (i.e., processable) intermediates are required.

The need for soluble or fusible precursors whose pyrolysis will give the desired ceramic material has led to a new area of macromolecular science, that of preceramic

polymers [3]. Such polymers are needed for a number of different applications. Ceramic powders by themselves are difficult to form into bulk bodies of complex shape. Although ceramists have addressed this problem using the more conventional ceramics techniques with some success, preceramic polymers could, in principle, serve in such applications, either as the sole material from which the shaped body is fabricated or as a binder for the ceramic powder from which the shaped body is to be made. In either case, pyrolysis of the green body would then convert the polymer to a ceramic material, hopefully of the desired composition. In the latter alternative, shrinkage during pyrolysis should not be great.

Ceramic fibers of diverse chemical compositions are sought for application in the production of metal-, ceramic-, glass- and polymer-matrix composites[4]. The presence of such ceramic fibers in a matrix, provided they have the right length-to-diameter ratio and are distributed uniformly throughout the matrix, can result in very considerable increases in the strength (i.e., fracture toughness) of the resulting material. To prepare such ceramic fibers, a suitable polymeric precursor is needed, one which can be spun by melt-spinning, dry-spinning, or wet-spinning techniques into fibers which then can be pyrolyzed (with or without a prior cure step).

Some materials with otherwise very useful properties such as high thermal stability and great strength and toughness are unstable with respect to oxidation at high temperatures. An example of such a class of materials is that of the carbon-carbon-composites. If these materials could be protected against oxidation by infiltration of their pores and the effective coating of their surface by a polymer whose pyrolysis gives an oxidation-resistant ceramic material, then one would have available new dimension of applicability of such carbon-carbon composite materials.

In order to have a useful preceramic polymer, considerations of structure and reactivity are of paramount importance. Not every inorganic or organometallic polymer will be a useful preceramic polymer. Some more general considerations merit discussion. Although preceramic polymers are potentially "high value" products if the desired properties result from their use, the more generally useful and practical systems will be those based on commercially available, relatively cheap starting monomers. Preferably, the polymer synthesis should involve simple, easily effected chemistry which proceeds in high yield. The preceramic polymer itself should be liquid or, if a solid, it should be fusible and/or soluble in at least some organic solvents, i.e., it should be processable. Its pyrolysis should provide a high yield of ceramic residue and the pyrolysis volatiles preferably should be non-hazardous and non-toxic. In the

requirement of high ceramic yield* economic considerations are only secondary. If the weight loss on pyrolysis is low, shrinkage will be minimized as will be the destructive effects of the gases evolved during the pyrolysis.

There are important considerations as far as the chemistry is concerned. First, the design of the preceramic polymer is of crucial importance. Many linear organometallic and inorganic polymers, even if they are of high molecular weight, decompose thermally by formation and evolution of small cyclic molecules, and thus the ceramic yield is low. In such thermolyses, chain scission is followed by "backbiting" of the reactive terminus thus generated at a bond further along the chain. Thus high molecular weight, linear poly(dimethylsiloxanes) decompose thermally principally by extruding small cyclic oligomers, $(\text{Me}_2\text{SiO})_n$, $n = 3, 4, 5, \dots$. When a polymer is characterized by this type of thermal decomposition, the ceramic yield will be low and it will be necessary to convert the linear polymer structure to a highly cross-linked one by suitable chemical reactions prior to its pyrolysis. In terms of the high ceramic yield requirement, the ideal preceramic polymer is one which has functional substituent groups which will give an efficient thermal cross-linking process so that on pyrolysis non-volatile networks (which lead to maximum weight retention) are formed. Thus, preceramic polymer design requires the introduction of reactive or potentially reactive functionality.

In the design of preceramic polymers, achievement of the desired elemental composition in the ceramic obtained from them (SiC and Si_3N_4 in the present cases) is a major problem. For instance, in the case of polymers aimed at the production of SiC on pyrolysis, it is more usual than not to obtain solid residues after pyrolysis which, in addition to SiC , contain an excess either of free carbon or free silicon. In order to get close to the desired elemental composition, two approaches have been found useful in our research: (1) the use of two comonomers in the appropriate ratio in preparation of the polymer, and (2) the use of chemical or physical combinations of two different polymers in the appropriate ratio.

Preceramic polymers intended for melt-spinning require a compromise. If the thermal cross-linking process is too effective at relatively low temperatures (100-200°C), then melt-spinning will not be possible since heating will induce cross-linking and will produce an infusible material prior to the spinning. A less effective cross-

* Ceramic yield is defined as:

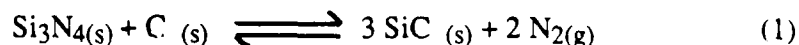
$$\frac{\text{weight of pyrolysis residue}}{\text{weight of material pyrolyzed}} \times 100$$

It thus represents the yield of the desired ceramic material plus that of any solid by-products.

linking process is required so that the polymer forms a stable melt which can be extruded through the holes of the spinneret. The resulting polymer fiber, however, must then be "cured", i.e., cross-linked, chemically or by irradiation, to render it infusible so that the fiber form is retained on pyrolysis. Finally, there still are chemical options in the pyrolysis step. Certainly, the rate of pyrolysis, i.e., the time/temperature profile of the pyrolysis, is extremely important. However, the gas stream used in the pyrolysis also is of great importance. One may carry out "inert" or "reactive" gas pyrolyses. An example of how one may in this way change the nature of the ceramic product is provided by one of our preceramic polymers which will be discussed in more detail later in this paper. This polymer, of composition $[(CH_3SiH_2NH)_a(CH_3SiN_b)_m]$, gives a black solid, a mixture of SiC, Si₃N₄, and some free carbon, on pyrolysis to 1000°C in an inert gas stream (nitrogen or argon). However, when the pyrolysis is carried out in a stream of ammonia, a white solid remains which usually contains less than 0.5% total carbon and is essentially pure silicon nitride. At higher temperatures (>400°C), the NH₃ molecules effect nucleophilic cleavage of the Si-C bonds present in the polymer and the methyl groups are lost as CH₄. Such chemistry at higher temperatures can be an important and sometimes useful part of the pyrolysis process.

Different chemistry, i.e., ligand displacement, is involved in another example of reactive gas pyrolysis from our boron ceramics project [5]. Polymers of type $[B_{10}H_{12}\text{-diamine}]_x$ (diamine = ethylene diamine and its N-methyl derivatives) give a mixture of B₄C, BN and a small amount of carbon as a black residue on pyrolysis under argon. When the pyrolysis is carried out in a stream of ammonia, a white residue, nearly pure boron nitride, is obtained. In this case, NH₃ displaces the diamine and thermal decomposition of the resulting B₁₀H₁₂·2NH₃ adduct results in the formation of BN. In a further example from our research, pyrolysis of Me₂N-terminated polymers of type $[Ti(NR)_2]_x$ give golden-yellow TiN on pyrolysis in a stream of ammonia; in a stream of argon, a black titanium carbonitride results [6].

In the pyrolysis of a preceramic polymer, the maximum temperature used is important. If it is too low, residual functionality (C-H, N-H, Si-H bonds in the case of polysilazanes) will still be present. On the other hand, too high a pyrolysis temperature can be harmful because of solid state reactions that can take place. For instance, if the polysilazane-derived silicon carbonitride contains a large amount of free carbon, a high temperature reaction between carbon and silicon nitride (eq. 1) [7] is a possibility.



The study of the pyrolysis products of preceramic polymers is not always straightforward. If crystalline species are produced (e.g., SiC and Si₃N₄ in the case of polysilazanes), then their identification by X-ray diffraction presents no problems. However, in many cases the pyrolysis products are amorphous. For instance, the polysilazane-derived silicon carbonitride mentioned above crystallizes only when it is heated above 1450°C and its characterization is difficult. Elemental analysis poses problems, in part because the pyrolysis product is very porous. As a result of its high surface area, it adsorbs moisture and volatiles very readily, so improper prior handling and preparation for analysis can result in misleading results. Solid state NMR spectroscopy is not routinely applicable to the study of such polymer-derived amorphous materials. In the case of our polysilazane pyrolysis product the material was paramagnetic and gave a strong ESR signal. A ²⁹Si NMR spectrum could not be obtained under experimental conditions which served well in obtaining a solid state ²⁹Si NMR spectrum of crystalline β-SiC. Although it is convenient to translate the elemental analysis of such amorphous silicon carbonitride materials into compositions comprising Si₃N₄, SiC and free carbon, this is misleading. At this stage carbon and nitrogen atoms (and oxygen atoms, if present) are bonded randomly to silicon in a three-dimensional covalent structure, according to Raman, ²⁹Si NMR and electron microscopy data obtained by the Dow Corning group for their hydridopolysilazane-derived pyrolysis product [8]. (The Dow Corning preceramic "HPZ" polysilazane is different from ours, being based on the reaction of HSiCl₃ with (Me₃Si)₂NH; note that these workers were able to obtain a solid state ²⁹Si NMR spectrum of their amorphous pyrolysis product). Our amorphous silicon carbonitride was converted to crystalline material when it was heated to 1490°C and X-ray diffraction lines due to α-Si₃N₄ and β-SiC were observed.

The first useful organosilicon preceramic polymer, a silicon carbide fiber precursor, was developed by S. Yajima and his coworkers at Tohoku University in Japan [9] and the fiber is manufactured by Nippon Carbon Co. as Nicalon®. As might be expected on the basis of the 2 C/1 Si ratio of the (CH₃)₂SiCl₂ starting material used in this process the ceramic fibers contain free carbon as well as silicon carbide. A typical analysis [9] showed a composition 1 SiC/0.78 C/0.22 SiO₂. (The latter is introduced in

the oxidative cure step of the polycarbosilane fiber). The Yajima polycarbosilane, while it was one of the first, is not the only polymeric precursor to silicon carbide which has been developed. Another useful system which merits mention is the polycarbosilane which resulted from research carried out by C. L. Schilling and his coworkers in the Union Carbide Laboratories in Tarrytown, New York [10]. More recently, a useful polymeric precursor for silicon nitride, already mentioned above, has been developed by workers at Dow Corning Corporation [8].

NEW SILICON-BASED PRECERAMIC POLYMER SYSTEMS: RESEARCH AT M.I.T.

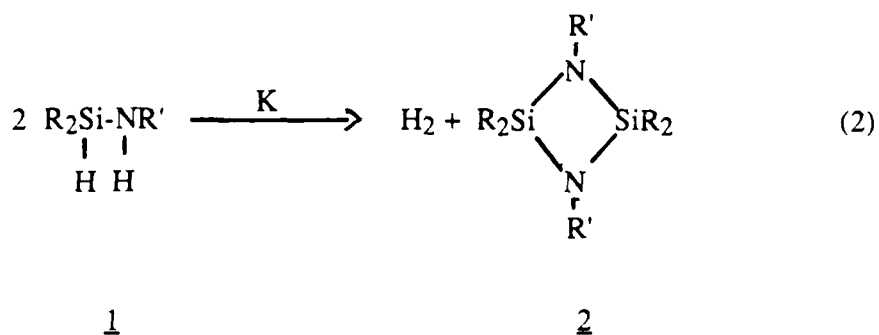
Our initial research on silicon-based preceramic polymers was aimed at developing a precursor for silicon nitride. To this end, we studied the ammonolysis of dichlorosilane, H_2SiCl_2 [11]. This reaction had already been carried out on a mmole scale in the gas phase and in benzene solution by Stock and Somieski in 1921 [12]. We found that this reaction gave a much better yield of soluble ammonolysis products when it was carried out in more polar solvents such as dichloromethane or diethyl ether [11]. The ammonolysis product, isolated as a mobile oil, deviated (by elemental analysis and proton NMR spectroscopy) from the ideal composition $(\text{H}_2\text{SiNH})_n$, being low in N and high in Si. Although this oil is stable indefinitely under nitrogen at -30°C , at room temperature it loses ammonia with resulting cross-linking to form a clear, insoluble glass. Its pyrolysis in a stream of nitrogen to 1150°C left a residue of $\alpha\text{-Si}_3\text{N}_4$ (by X-ray diffraction) in about 70% ceramic yield. Although the H_2SiCl_2 ammonolysis product did not appear to be stable at room temperature (under nitrogen) as the neat liquid, it was stable in solution, so it seemed possible that polysilazane fibers might be accessible via dry spinning in a suitable organic solvent. Also, one might expect such ammonolysis product solutions could be used in the preparation of silicon nitride coatings and for the infiltration of porous bodies. Nevertheless, we did not pursue this research direction, mainly because H_2SiCl_2 is a potentially dangerous compound, as tests carried out on behalf of Dow Corning had shown [13]. In independent studies, workers at the Toa Nenryo Kogyo Company in Japan [14] carried out the ammonolysis of the known H_2SiCl_2 /pyridine adduct. Their product, obtained as a viscous oil or a resinous solid, also underwent cross-linking at room temperature and gave $\alpha\text{-Si}_3\text{N}_4$ and elemental silicon on pyrolysis to 1300°C .

In our continuing research we compromised, replacing one of the hydrogen substituents of H_2SiCl_2 by a methyl group, i.e., using $\text{CH}_3\text{SiHCl}_2$ as our starting material. Using this commercially available, relatively cheap and safe chlorosilane, we have developed a novel process for the preparation of useful polymeric precursors for silicon carbonitrides and, ultimately, $\text{Si}_3\text{N}_4/\text{SiC}$ mixtures [15].

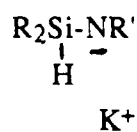
The ammonolysis of $\text{CH}_3\text{SiHCl}_2$ has been reported to give a mixture of cyclic and (possibly) linear oligomers, $[\text{CH}_3\text{SiHNNH}]_n$ [16]. The ammonolysis product, after removal of the precipitated NH_4Cl which also is produced, can be isolated as a clear, mobile liquid in high yield. Its C, H and N analysis and its spectroscopic (^1H NMR, IR) data are in agreement with the $[\text{CH}_3\text{SiHNNH}]_n$ formulation. Molecular weight determinations (cryoscopy in benzene) of several preparations ranged from 280-320 g/mol ($x = 4.7-5.4$). The product is quite stable at room temperature, but it is sensitive to moisture and must be protected from the atmosphere. This mixture of $[\text{CH}_3\text{SiHNNH}]_n$ oligomers is not suitable for ceramics preparation without further processing. On pyrolysis to 1000°C in a stream of nitrogen the ceramic yield is only 20%, so it was necessary to convert these cyclic $[\text{CH}_3\text{SiHNNH}]_x$ oligomers to material of higher molecular weight.

The conversion of the cyclopolysilazanes obtained by ammonolysis of diorganodichlorosilanes to materials of higher molecular weight was investigated by Krüger and Rochow some years ago when there was interest in polysilazanes as polymers in their own right [17]. We applied their procedure, the thermal, ammonium salt-induced polymerization, which in the case of hexamethylcyclotrisilazane appears to give polymers containing both linear and cyclic components, to the $\text{CH}_3\text{SiHCl}_2$ ammonolysis product. A very viscous oil of higher molecular weight was produced but the ceramic yield obtained on pyrolysis was a disappointing 36%.

The solution to our problem of converting the $[\text{CH}_3\text{SiHNNH}]_n$ cyclics to a useful preceramic polymer was provided by earlier workers [18] who had described the conversion of silylamines of type **1** to cyclodisilazanes, **2**, in high yield by the action of potassium in di-*n*-butyl ether (eq. 2). In this dehydrocyclodimerization (DHCD) reaction, the potassium serves to metallate the NH functions to give **3**. This then either



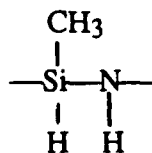
eliminates H^- from silicon to give an intermediate with a silicon-nitrogen double



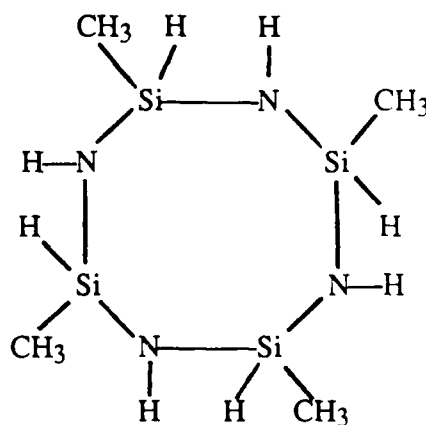
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bond, $\text{R}_2\text{Si}=\text{NR}'$, which then undergoes head-to-tail dimerization to form 2, or alternatively, reacts with a molecule of $\text{R}_2\text{Si}(\text{H})\text{NHR}'$ to give an intermediate which undergoes cyclization to 2 with displacement of H^- .

The repeating unit in the $[\text{CH}_3\text{SiH}_2\text{NH}]_n$ cyclics is 4. For example, the cyclic

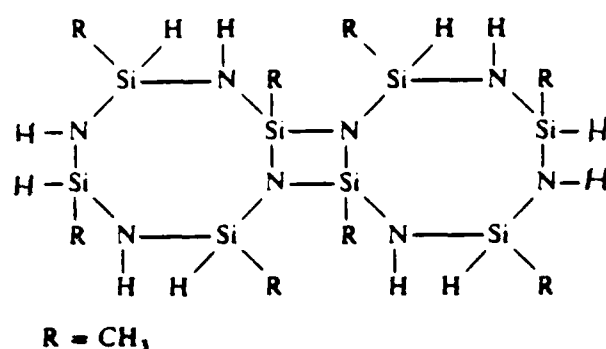


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tetramer is the 8-membered ring compound 5. On the basis of equation 2, the adjacent NH and SiH groups provide the functionality which permits the molecular weight of the $[\text{CH}_3\text{SiH}_2\text{NH}]_n$ cyclics to be increased. Thus, two $[\text{CH}_3\text{SiH}_2\text{NH}]_n$ cyclics may be expected to be linked together via a four-membered ring as shown in 6. However, six



6

$\text{Si}(\text{H})\text{-N}(\text{H})$ units remain in 6, so, in principle, there is a possibility of extensive further linking together of the species contained in the $[\text{CH}_3\text{SiH}_2\text{NH}]_n$ product of $\text{CH}_3\text{SiHCl}_2$ ammonolysis.

Treatment of a solution of the $\text{CH}_3\text{SiHCl}_2$ ammonolysis product, cyclo- $[\text{CH}_3\text{SiH}_2\text{NH}]_n$, with a catalytic amount of a base (generally an alkali metal base) strong enough to deprotonate the N-H function in a suitable solvent results in immediate evolution of hydrogen. We believe that a sheet-like network polymer (which, however, is not flat) having the general functional unit composition $[(\text{CH}_3\text{SiH}_2\text{NH})_a(\text{CH}_3\text{SiN})_b(\text{CH}_3\text{SiHNK})_c]_n$ is formed. When hydrogen evolution ceases, a "living" polymer with reactive silylamide functions is present. On reaction of the latter with an electrophile (CH_3I or a chlorosilane), a neutral polysilazane is formed and can be isolated in essentially quantitative yield. In our experiments we generally have used

catalytic amounts of potassium hydride (1-4 mole %, based on $\text{CH}_3\text{SiH}_2\text{NH}$) as a base. When THF was used as reaction solvent, the product was isolated, after addition of CH_3I , in the form of a white powder (average molecular weight, 1180) which was found to be soluble in hexane, benzene, diethyl ether, THF, and other common organic solvents. It is imperative to exclude atmospheric moisture since the $[\text{CH}_3\text{SiH}_2\text{NH}]_n$ cyclics are readily hydrolyzed. The product polymer on the other hand, is of greatly diminished sensitivity to hydrolysis.

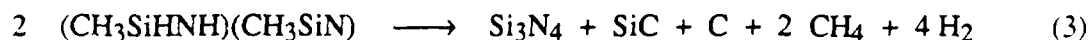
The composition of the polysilazane product of an experiment of the kind detailed above, ascertained by proton NMR spectroscopy, was $(\text{CH}_3\text{SiH}_2\text{NH})_{0.39}(\text{CH}_3\text{SiN})_{0.57}(\text{CH}_3\text{SiHNCH}_3)_{0.04}$ and its combustion analysis (C, H, N, Si) agreed with this formulation. These results are compatible with a process in which $(\text{CH}_3\text{SiH}_2\text{NH})_n$ rings are linked together via Si_2N_2 bridges as shown in 6. The experimental $(\text{CH}_3\text{SiN})/(\text{CH}_3\text{SiH}_2\text{NH})$ ratio of ~ 1.3 indicates that further linking via Si_2N_2 rings must have taken place.

Whatever the structure of the silazane polymers obtained by KH treatment of the $[\text{CH}_3\text{SiH}_2\text{NH}]_n$ cyclics, these polymers are excellent ceramic precursors. Examination of the polymers from various preparations by TGA showed the weight loss on pyrolysis to be only between 15 and 20%. The pyrolysis appears to take place in three steps: a 3-5% weight loss (involving evolution of H_2) from 100°C to 350°C ; a 2% weight loss from 350 - 550°C and a 9% weight loss from 550°C to 900°C . During the 550 - 900°C stage a mixture of H_2 and methane was evolved. A trace of ammonia, in addition to H_2 was lost between 350 and 550°C .

In typical bulk pyrolysis experiment, pyrolysis was conducted under a slow stream of nitrogen. The sample was heated quickly to 500°C and then slowly over 8 h to 1420°C and was held at 1420°C for 2 h. The ceramic powder was a single body and black. Powder X-ray diffraction ($\text{CuK}\alpha$ with Ni filter) showed only very small, broad peaks for $\alpha\text{-Si}_3\text{N}_4$. (At 1490°C , lines due to $\beta\text{-SiC}$ also appeared). Scanning electron microscopy analysis showed little discernible microstructure with only a few very fine grains appearing at high magnification. The bulk appearance of the ceramic suggested that pyrolysis took place after the polymer had melted. There were many large holes and craters where the liquid bubbles apparently had burst. In such experiments ceramic yields usually were between 80 and 85%. The polysilazane used in the experiment above had been prepared in diethyl ether. It had a molecular weight of around 900 and went through a melt phase when it was heated. This could be shown when it was heated in a sealed capillary: it began to soften around 65°C , becoming more fluid with

increasing temperature. The polysilazane prepared in THF generally is of higher molecular weight (MW = 1700-2000) and does not soften when heated to 350°C. It gave an 83% yield of a black ceramic material on pyrolysis under nitrogen to 1000°C.

The pyrolysis of the silazane polymer may be represented by eq. 3. Here the ceramic yield ($\text{Si}_3\text{N}_4 + \text{SiC} + \text{C}$) would be 83 wt%. An analysis of such a ceramic



product gave 12.87% C, 26.07% N, and 59.52% Si. This analysis is compatible with eq. 3 and leads to a formal ceramic constitution, based on the 4 Si of eq. 2, of 0.88 Si_3N_4 , 1.27 SiC, 0.75 C, or on the basis of weight per cent, 67% Si_3N_4 , 28% SiC and 5% carbon.

Thus the chemistry leading to the desired ceramic product is quite satisfactory: most of the requirements mentioned earlier are met. Initial evaluation of the polysilazane shows it to have promise in three of the main potential applications of preceramic polymers: in the preparation of ceramic fibers and of ceramic coatings and as a binder for ceramic powders.

Isostatically pressed (40,000 psi) bars of the polymer on pyrolysis to 1100°C gave a coherent, rectangular ceramic bar which had not cracked or bloated and could not be broken by hand.

In collaboration with ceramists at the Celanese Research Company it was found that our "meltable" polysilazane cannot be melt-spun. Apparently, the thermal cross-linking process which is so effective in giving a high ceramic yield on pyrolysis takes place in the heated chamber of the spinning machine and quickly gives infusible polymer. However, these polysilazanes can be dry-spun. In this process the solid polysilazane is dissolved in an appropriate solvent and then is extruded through a spinneret into a heated drying chamber in which the solvent is volatilized, leaving the solid polymer fiber. These polymer fibers could be pyrolyzed to give ceramic fibers. (No cure-step is required.) In simpler experiments, it was shown that fibers one to two feet in length could be drawn from the sticky, waxy solid which remained when a toluene solution of the polysilazane was evaporated. Pyrolysis of these fibers under nitrogen produced long, flexible black fibers.

Our polysilazane also serves well as a binder for ceramic powders. The preparation of such composites (using commercial samples of fine α -SiC, β -SiC and α -

Si_3N_4 of 0.36-0.4 μm mean particle size) required appropriate dispersion studies. The ceramic powder was dispersed in a solution of toluene containing the appropriate weight of polysilazane and then the toluene was evaporated using a rotary evaporator, leaving a waxy residue. Vacuum distillation removed the remaining solvent and left chunks of solid material. These were finely ground and pressed into a bar at 5000 psi. Isostatic pressing to 40,000 psi followed and then the bars were pyrolyzed in a tube furnace under nitrogen (10°C a minute, to 1100°C). The maximum density (~ 2.4 g/cc) was achieved in these experiments with a polymer loading of 30%.

As mentioned, our polysilazane undergoes thermal cross-linking too readily to permit melt-spinning. It was clear that if melt-spinning was to be successful we would have to prepare a less reactive polysilazane with fewer reactive $\text{Si}(\text{H})\text{-N}(\text{H})$ groups. To achieve this, we have studied polysilazanes derived by the dehydrocyclodimerization of the products of coammonolysis of $\text{CH}_3\text{SiHCl}_2$ and $\text{CH}_3(\text{Un})\text{SiCl}_2$, where Un is an unsaturated substituent such as vinyl, $\text{CH}_2=\text{CH}$, or allyl, $\text{CH}_2\text{CH}=\text{CH}_2$. These groups were used because a melt-spun fiber requires a subsequent cure step to render it infusible. If this is not done, the fiber would simply melt on pyrolysis and no ceramic fiber would be obtained. The vinyl and allyl groups provide $\text{C}=\text{C}$ functionality which can undergo UV-catalyzed Si-H additions, reactions which after melt-spinning in principle should lead to extensive further cross-linking without heating.

To provide the required monomers, we ammonolyzed mixtures of $\text{CH}_3\text{SiHCl}_2$ and $\text{CH}_3(\text{CH}_2=\text{CH})\text{SiCl}_2$ and $\text{CH}_3\text{SiHCl}_2$ and $\text{CH}_3(\text{CH}_2=\text{CHCH}_2)\text{SiCl}_2$, respectively. The $[(\text{CH}_3\text{SiHNH})_x(\text{CH}_3(\text{Un})\text{SiNH})_y]_n$ oligomers were prepared using $\text{CH}_3\text{SiHCl}_2/\text{CH}_3(\text{Un})\text{SiCl}_2$ ratios of 3, 4 and 6, although other ratios can be used. This gives materials which still contain many $(\text{CH}_3)\text{Si}(\text{H})\text{-N}(\text{H})$ - units, so polymerization by means of the process of eq. 2 still will be possible. However, dilution of the ring systems of the cyclic oligomers with $\text{CH}_3(\text{Un})\text{Si}$ units will decrease the cross-linking which will occur on treatment with the basic catalyst.

The coammonolysis of $\text{CH}_3\text{SiHCl}_2$ and $\text{CH}_3(\text{Un})\text{SiCl}_2$ in the indicated ratios was carried out by the procedure as described for ammonolysis of $\text{CH}_3\text{SiHCl}_2$ [15]. A mixture of mixed cyclic oligomeric silazanes is to be expected in these reactions, $[(\text{CH}_3(\text{H})\text{SiNH})_x(\text{CH}_3(\text{Un})\text{SiNH})_y]_n$, with more than one ring size present. In each preparation, the soluble, liquid products were isolated and used in the base-catalyzed polymerizations. When a ratio $\text{CH}_3\text{SiHCl}_2/\text{CH}_3(\text{Un})\text{SiCl}_2$ of $x:1$ ($x>1$) was used in the ammonolysis reaction the $\text{CH}_3(\text{H})\text{Si}/\text{CH}_3(\text{Un})\text{Si}$ ratio in the soluble ammonolysis product usually was somewhat less than $x:1$.

The addition of the various ammonolysis products to suspensions of catalytic amounts of KH in dry tetrahydrofuran resulted in hydrogen gas evolution with formation of a clear solution. Thermal treatment was followed by treatment with methyl iodide to "kill" the "living" polymeric potassium silylamide present in solution. The resulting polysilazane generally was obtained in high (90%) yield and these products, always white powders, were soluble in organic solvents such as hexane, benzene, toluene and THF. Their average molecular weights were in the 800 -1200 range. The presence of unchanged vinyl and allyl groups was proven by the IR and ^1H NMR spectra. A typical elemental analysis led to the empirical formula $\text{SiC}_{1.5}\text{NH}_{4.4}$ which could be translated into a composition $[(\text{CH}_3\text{SiHNNH})(\text{CH}_3(\text{CH}_2=\text{CH})\text{SiNH})(\text{CH}_3\text{SiN})_{2.3}]_x$.

These polysilazanes, upon pyrolysis to 1000°C under argon or nitrogen, gave black ceramic materials in good yield (73-86%, by weight). Analysis of the ceramic produced by such pyrolysis of one of these polysilazanes gave a formal composition 67.5 wt.% Si_3N_4 , 22.5 wt.% SiC, and 10.0 wt.% unbound carbon. UV irradiation curing of fibers formed from these vinyl-or allyl-containing polysilazanes was possible. The following experiment shows this. Fibers were pulled from a concentrated syrup of a polysilazane derived from a 4:1 molar ratio $\text{CH}_3\text{SiHCl}_2/\text{CH}_3(\text{CH}_2=\text{CH})\text{SiCl}_2$ coammonolysis product by DHCD in THF. Some fibers were pyrolyzed without any further treatment. These melted in large part, leaving very little in the way of ceramic fibers. Other fibers were subjected to UV irradiation for 2 hours. These, on pyrolysis under argon, did not melt and ceramic fibers were obtained. This polysilazane thus is a good candidate for melt-spinning.

In order to obtain a SiC/ Si_3N_4 mixture rich in Si_3N_4 by the preceramic polymer route, one requires a polymer which is richer in nitrogen than the $\text{CH}_3\text{SiHCl}_2$ ammonolysis product, $[\text{CH}_3\text{SiHNNH}]_n$. In designing such a preceramic polymer, one would like to retain the facile chemical and thermal cross-linking system which the Si(H)-N(H)-unit provides. We have found that the coammonolysis of $\text{CH}_3\text{SiHCl}_2$ and HSiCl_3 serves our purposes well. For HSiCl_3 , ammonolysis introduces three Si-N bonds per silicon atom, so the ammonolysis product of $\text{CH}_3\text{SiHCl}_2/\text{HSiCl}_3$ mixtures will contain more nitrogen than the ammonolysis product of $\text{CH}_3\text{SiHCl}_2$ alone [19].

In order to define the optimum system, we have investigated the ammonolysis of $\text{CH}_3\text{SiHCl}_2/\text{HSiCl}_3$ mixtures in various ratios in two solvents, diethyl ether, and tetrahydrofuran (THF). $\text{CH}_3\text{SiHCl}_2/\text{HSiCl}_3$ mol ratios of 6, 3 and 1 were examined. In both solvents, the 6:1 and 3:1 ratios produced polysilazane oils with molecular

weights in the range 390-401 g/mol and 480 g/mol, respectively. When a 1:1 reactant ratio was used, waxes of somewhat higher (764-778 g/mol) molecular weights were obtained in both solvents. In the 1:1 reaction carried out in Et₂O the yield of soluble product was only 40% but in THF it was nearly quantitative.

The oils produced in the 6:1 and 3:1 reactions in Et₂O appeared to be stable on long-term storage at room temperature in the absence of moisture. However, the waxy product of 1:1 (Et₂O) reactions and all the coammonolysis products prepared in THF formed gels (i.e., became insoluble) after 3-4 weeks at room temperature, even when stored in a nitrogen-filled dry box.

The pyrolysis of the coammonolysis products was studied. The 6 CH₃SiHCl₂/1 HSiCl₃ ammonolysis product would be the least cross-linked since it contains the least amount of trifunctional component and, as expected, low ceramic yields were obtained on pyrolysis of these products. Pyrolysis of the 3:1 products gave increased ceramic yields, while pyrolysis of the most highly cross-linked 1:1 ammonolysis products gave quite good ceramic yields, 72% for the product prepared in Et₂O, 78% for that prepared in THF.

All of the ammonolysis products were submitted to the KH-catalyzed dehydrocyclodimerization reaction in order to obtain more highly cross-linked products that would give higher ceramic yields on pyrolysis. In all cases, the standard procedure [15] was used (1% KH in THF, followed by quenching with CH₃I (or a chlorosilane)). In every reaction, the product was a white solid which was produced in virtually quantitative yield. The proton NMR spectra of these products, as expected, showed an increase in the SiCH₃/SiH + NH proton ratio, while the relative SiH/NH ratio was unchanged. In all cases, the molecular weights of the solid products were at least double that of the starting ammonolysis product, so the desired polymerization had occurred. Although the increase in molecular weight in these DHCD reactions is not great, any increase is useful for further processing. The reactions bring the advantage that the oils are converted to more easily handleable solids.

Pyrolysis of the white solids obtained in these KH-catalyzed dehydrocyclodimerization reactions (under argon from 50-950°C) produced black ceramic residues, with the exception of the 1:1 THF ammonolysis-derived solid which left a brown residue. The ceramic yields were excellent (all greater than or equal to 82%, with the highest being 88%).

Analysis of bulk samples of the ceramic materials produced in the pyrolysis of the various KH-catalyzed dehydrocyclodimerization products showed that our goal of a

higher formal $\text{Si}_3\text{N}_4/\text{SiC}$ ratio had been achieved: for the 1:1 ammonolysis product-derived polymers, 86% Si_3N_4 , 8% SiC and 5% C (THF ammonolysis) and 83% Si_3N_4 , 11% SiC and 6% C (Et_2O ammonolysis); for the 3:1 and 6:1 ammonolysis product derived polymers: 77% Si_3N_4 , 18-19% SiC and 4-5% C (Et_2O ammonolysis) and 74% Si_3N_4 , 20% SiC and 5-6% C (THF ammonolysis).

These polymers may be used in the preparation of quite pure silicon nitride if the pyrolysis is carried out in a stream of ammonia (a reactive gas) rather than under nitrogen or argon. Thus pyrolysis of the dehydrocyclodimerization product of the 1:1 (THF) ammonolysis product to 1000°C in a stream of ammonia gave a white ceramic residue in high yield which contained only 0.29% C, the remainder being silicon nitride.

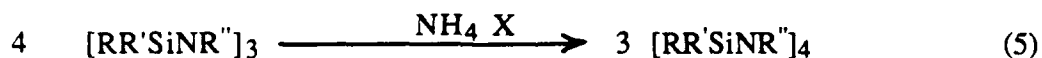
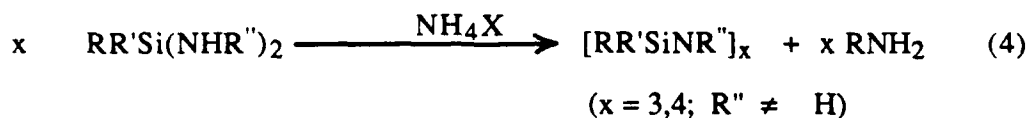
Other commercially available RSiCl_3 compounds are CH_3SiCl_3 (a cheap byproduct of the Direct Process) and $\text{CH}_2=\text{CHSiCl}_3$ (also an inexpensive starting material) and both were included in this study. In both cases, 6:1, 3:1; and 1:1 $\text{CH}_3\text{SiHCl}_2/\text{RSiCl}_3$ ammonolysis products were prepared and submitted to the dehydrocyclodimerization procedure. The ceramic yields obtained on pyrolysis of the resulting polymers were high. In the $\text{CH}_3\text{SiHCl}_2/\text{CH}_3\text{SiCl}_3$ experiments: 78-86%. In all cases, a black ceramic residue resulted when the pyrolysis to 1000°C was carried out in a stream of argon. As expected, the carbon content (in the form of SiC and free C) was higher than that of the $\text{CH}_3\text{SiHCl}_2/\text{HSiCl}_3$ -derived ceramic: 12-18% SiC, up to 9.5% C. Nonetheless, higher Si_3N_4 contents than those obtained when $\text{CH}_3\text{SiHCl}_2$ is used alone (~67%) were obtained: 76-80% Si_3N_4 . To produce a ceramic material containing only Si_3N_4 , the solid polysilazane derived from DHCD of the oil obtained by ammonolysis of 6:1 $\text{CH}_3\text{SiHCl}_2/\text{CH}_3\text{SiCl}_3$ was pyrolyzed in a stream of ammonia (to 1000°C). A white ceramic residue containing only 0.36% by weight C resulted.

With 6:1, 3:1 and 1:1 $\text{CH}_3\text{SiHCl}_2/\text{CH}_2=\text{CHSiCl}_3$ ammonolysis products DHCD gave white solids whose pyrolysis resulted in increased carbon content and decreased Si_3N_4 (vs the $\text{CH}_3\text{SiHCl}_2/\text{CH}_3\text{SiCl}_3$ examples): 69-73% Si_3N_4 , 9-13% SiC, 12-18% C (by weight).

We have also investigated another approach to mixed systems of the type discussed above: the copolymerization of oligomeric cyclopolysilazanes and of alkylaminosilanes with the $\text{CH}_3\text{SiHCl}_2$ ammonolysis product, $[\text{CH}_3\text{SiHNNH}]_n$, followed by dehydrocyclodimerization. This approach is based on the ring-opening polymerization of cyclic oligosilazanes of Krüger and Rochow [17] mentioned above. In this process, the cyclic ammonolysis products (n mainly 3 and 4) were heated with a catalytic amount of an ammonium halide, preferably NH_4Br or NH_4I , at temperatures

of 160°C or greater at atmospheric pressure for 6 - 8 hours. During the reaction, gaseous NH_3 was evolved and an oily polymer which contained silicon-halogen bonds was formed. The Si-X functions were removed by the treatment of the polymer with NH_3 in diethyl ether solution. The final products were described as colorless, waxy polysilazanes of molecular weight greater than 10,000. The structure of these polymers could not be determined with certainty, but linear and cyclic structural components were suggested. [17] The polymers obtained were soluble in organic solvents such as benzene, petroleum ether or carbon tetrachloride; they melted in the range 90-140°C and they were partly crystalline. The attempted NH_4Br -catalyzed copolymerization of a 4;1 mixture of $[(\text{CH}_3)_2\text{SiNH}]_3$ and $[(\text{CH}_3)(\text{CH}_2=\text{CH})\text{SiNH}]_4$ as described above gave an insoluble, colorless rubber [17].

Primary alkylaminosilanes and -silazanes also have been reported to undergo deamination (eq. 4) and ring equilibration (eq. 5) when heated with catalytic amounts of ammonium salts [20].



Such ammonium salt-catalyzed processes very likely proceed via reactive silylammonium intermediates which may be useful in other silazane-conversion processes. In order to obtain less highly functionalized polysilazanes suitable for melt-spinning, such ammonium salt-catalyzed processes were examined.

In the general procedure, the mixture of $[\text{CH}_3\text{SiHNNH}]_n$ and the silylamino or silazane compound is heated under an inert atmosphere (dry nitrogen or argon) in the presence of about 2 weight percent of an ammonium salt at temperatures around 155-170°C for 4.5 to 5 hours. During the reaction, ammonia and, in those cases where a -Si-NHR compound is the reaction partner, an amine (RNH_2) is evolved. The preferred ammonium salt is $(\text{NH}_4)_2\text{SO}_4$, but others, e.g., NH_4Cl , NH_4Br , etc., may

be used. The $(\text{NH}_4)_2\text{SO}_4$ is preferred because it is easily removed by filtration when, upon completion of the deamination reaction, the reaction mixture is diluted with THF.

The coreactants used in this study were $[\text{CH}_3\text{SiHNCH}_3]_n$ and $[\text{CH}_3(\text{CH}_2=\text{CH})\text{SiNH}]_n$ cyclics, $[\text{CH}_2=\text{CHSi}(\text{NH})_{1.5}]_n$, $\text{CH}_3(\text{CH}_2=\text{CH})\text{Si}(\text{NHCH}_3)_2$ and $[\text{HSi}(\text{NHCH}_3)\text{NCH}_3]_n$ cyclics. The ammonium salt-catalyzed deamination-crosslinking products were viscous liquids in the case of the diorganosilane derivatives, resinous waxes in the case of the mono-organosilane derivatives.

In an alternative procedure, rather than carrying out the ammonolysis of $\text{CH}_3\text{SiHCl}_2$ and $\text{CH}_3(\text{R})\text{SiCl}_2$ separately, an appropriate mixture of the two was treated with ammonia. The coammonolysis product then was heated with $(\text{NH}_4)_2\text{SO}_4$ at 170-185°C to give a soluble, cross-linked, partially deaminated product. (The coammonolysis product was a slightly viscous, colorless oil; the deaminated product ($T = 170\text{-}175^\circ\text{C}$) was a light yellow, viscous liquid.

The products of the $(\text{NH}_4)_2\text{SO}_4$ -catalyzed reactions of $[\text{CH}_3\text{SiHNH}]_n$ with other silazanes and aminosilanes all were subjected to the KH-catalyzed dehydrocyclodimerization reaction [15]. This served to convert the viscous liquids and waxes to soluble solids, as is generally the case when this procedure is applied to $\text{CH}_3\text{SiHCl}_2$ -derived polysilazane systems.

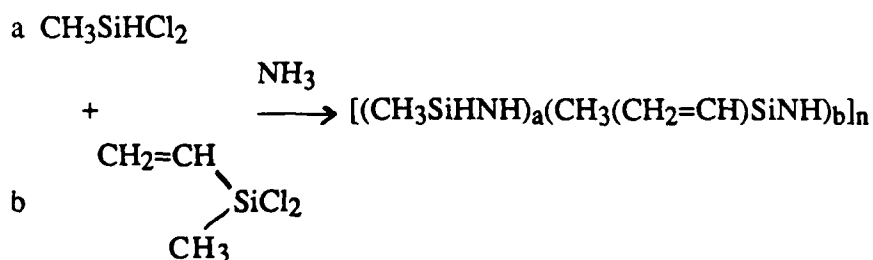
Each step of this sequence of $(\text{NH}_4)_2\text{SO}_4$ -catalyzed deamination/crosslinking and KH-catalyzed DHCD serves to increase the ceramic yield obtained on pyrolysis of the reaction product. For instance, the ceramic yield obtained from a 4:1 (by weight) blend of $[\text{CH}_3\text{SiHNH}]_n$ and $[\text{CH}_3(\text{CH}_2=\text{CH})\text{SiNH}]_n$ on pyrolysis (to 1000°C under argon) was 49%. This mixture, after it had been heated with 1.5 weight % $(\text{NH}_4)_2\text{SO}_4$ at 165°C for 4.5 hours was converted to a viscous liquid whose pyrolysis (same conditions) gave a ceramic yield of 69%. When this material in turn was treated with 1.3 weight % of KH in THF at room temperature (CH_3I quench), a solid product was obtained whose pyrolysis (to 1000°C) gave a ceramic yield of 83%. It may be noted that not only do the final solid "KH products" give a higher ceramic yield on pyrolysis, but they are less reactive toward atmospheric moisture and they are more readily handled than the "ammonium salt" products.

The increase in ceramic yield on going from the "ammonium

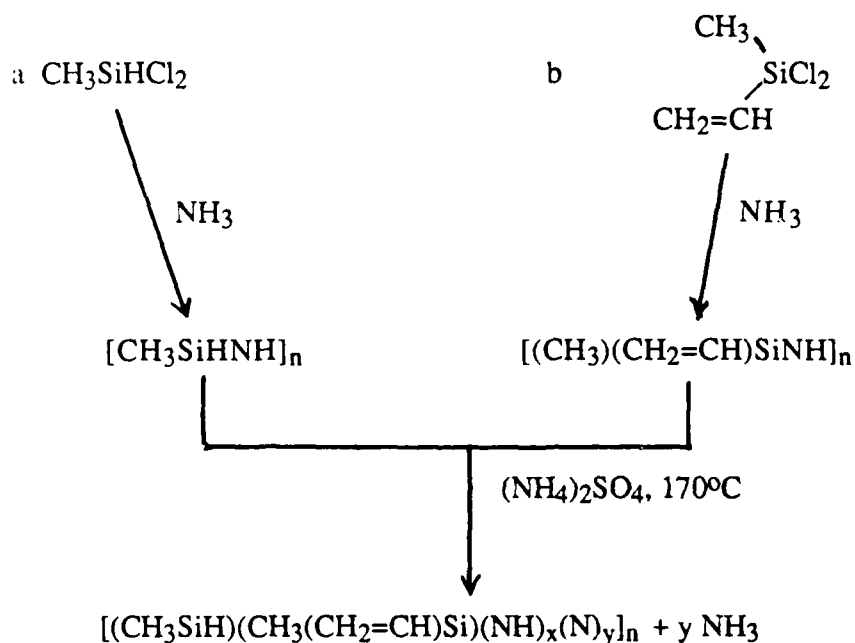
salt product" to the "KH product" was variable, depending on the other component used (in addition to $[\text{CH}_3\text{SiH}(\text{NH})]_n$) and the relative amounts of each used. In general, the greater the percentage of the other product in the mixture, the less was this increase in ceramic yield.

The nature of the ammonium salt-catalyzed deamination/crosslinking of silazanes and aminosilanes is not well understood. It is clear (by experiment) that NH_3 is evolved when $[\text{CH}_3(\text{R})\text{SiNH}]_n$ type silazanes participate in the reaction and CH_3NH_2 when methylaminosilanes or -silazanes are used. This would lead to some crosslinking through conversion of Si_2N units to Si_3N (e.g., $3 \text{ SiNHSi} \longrightarrow 2(\text{Si})_3\text{N} + \text{NH}_3$). Thus the function of the $(\text{NH}_4)_2\text{SO}_4$ catalyzed reaction in the present case is to "copolymerize", through such a deaminative crosslinking process, the two reactants. The product thus is not equivalent to the material obtained simply by coammonolysis. That is, the processes shown in Schemes 1 and 2 are not equivalent. The process in Scheme 2 gives a partially crosslinked product. In principle, a product with the same general constitution as that of Scheme 2 should be obtained by treating the product of Scheme 1 with a catalytic amount $(\text{NH}_4)_2\text{SO}_4$ at 170°C . However,

Scheme 1



Scheme 2



the detailed structure of the two products would not be expected to be the same.

A major objective of this work was the development of melt-spinnable polysilazanes. Such were provided by the $\text{CH}_3\text{SiH}/\text{CH}_3(\text{CH}_2=\text{CH})\text{Si}$ system, with the experimental approach either of Scheme 1 (followed by $(\text{NH}_4)_2\text{SO}_4$ -catalyzed deamination/crosslinking and KH-catalyzed crosslinking) or of Scheme 2 (followed by KH-catalyzed crosslinking) being used. In the Scheme 2 approach, 30 weight percent of either $[\text{CH}_3(\text{CH}_2=\text{CH})\text{SiNH}]_n$ or $\text{CH}_3(\text{CH}_2=\text{CH})\text{Si}(\text{NHCH}_3)_2$ was used along with the $\text{CH}_3\text{SiHCl}_2$ ammonolysis product, $[\text{CH}_3\text{SiHNNH}]_n$. Treatment of the product with 1.6 weight % of KH in THF at room temperature gave a white solid which had a softening temperature (by TMA) of 79-96°C and gave a 73% ceramic yield on pyrolysis to 1000°C under argon. The approach of Scheme 1, using 1 molar equivalent of $\text{CH}_3\text{SiHCl}_2$ and 0.3 of $\text{CH}_3(\text{CH}_2=\text{CH})\text{SiCl}_2$ gave a coammonolysis product which was treated first with 2 weight % of $(\text{NH}_4)_2\text{SO}_4$ at 170-185°C for 4 - 5 hours, then with 1.5 weight % of KH in THF at room temperature for 2.5 hours, to give as final product a white solid (TMA softening temperature 49-68°C, ceramic yield (to 1000°C under argon) 71%). On being heated, both of these solid products melted to a transparent liquid at 80 to 100°C. Decomposition or evolution of volatiles does not

appear to occur at temperatures below 160°C. Consistent with this observation is the TGA of these materials which shows weight loss starting at about 150°C. The final product of the Scheme 1 approach was heated to 165°C for 3 hours under nitrogen. After the melt had cooled to room temperature, the resulting glassy solid was still soluble in hexane, a fact which indicates that extensive thermal crosslinking had not taken place. It would seem that these products are good candidates for melt-spinning.

Fibers could be drawn from concentrated syrups of these products in toluene. These could not directly be converted to ceramic fibers (since they melted on being heated) and required a "cure" step to render them infusible. The required "cure" could be accomplished, as in the case discussed earlier, by UV irradiation of the fibers. Following this, their pyrolysis gave ceramic fibers: black when the pyrolysis was effected in a stream of argon, white when effected in a stream of ammonia.

The polysilazanes prepared from the systems discussed immediately above, on pyrolysis under argon to 1000°C, gave black ceramic products whose elemental analysis could be rationalized in terms of formal compositions (in weight %): 62-65% Si₃N₄, 15-20% SiC and 14-16% free carbon. The white materials obtained on pyrolysis in a stream of ammonia in general contained less than 1% carbon.

Our research also has been directed at SiC precursors. It began with an examination of a potential starting material in which the C:Si ration was 1, the ratio desired in the derived ceramic product. Available methylsilicon compounds with a 1 C/1 Si stoichiometry are CH₃SiCl₃ and CH₃SiHCl₂. The latter, in principle, could give [CH₃SiH]_n cyclic oligomers and linear polymers on reaction with an alkali metal. In practice, the Si-H linkages also are reactive toward alkali metals. Thus, mixed organochlorosilane systems containing some CH₃SiHCl₂ have been treated with metallic potassium by Schilling and Williams [21]. It was reported that the CH₃SiHCl₂-based contribution to the final product was (CH₃SiH)_{0.2}(CH₃Si)_{0.8}, i.e., about 80% of the available Si-H bonds had reacted. Such Si-H reactions lead to crosslinking in the product, or to formation of polycyclic species if cyclic products are preferred. Nevertheless, we have used this known reaction of CH₃SiHCl₂ with an alkali metal as an entry to new preceramic polymers [22].

When the reaction of CH₃SiHCl₂ with sodium pieces was carried out in tetrahydrofuran medium, a white solid was isolated in 48% yield. This solid was poorly soluble in hexane, somewhat soluble in benzene, and quite soluble in THF. Its ¹H NMR spectrum indicated that extensive reaction of Si-H bonds had occurred. The δ(SiH)/δ(SiCH₃) integration led to a constitution [CH₃SiH]_{0.4}(CH₃Si)_{0.6}]_n. Here the

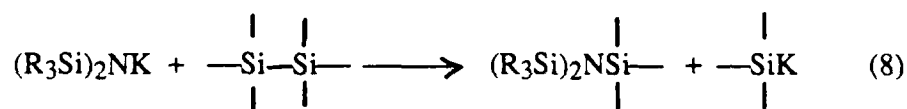
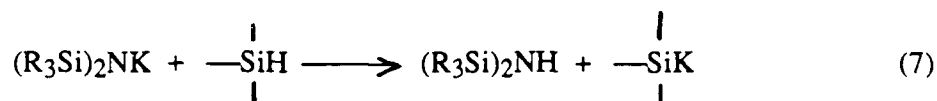
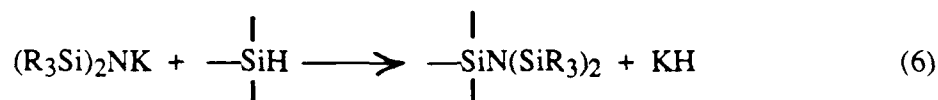
CH_3SiH units are ring and chain members which are not branching sites; the CH_3Si units are ring and chain members which are branching sites. In our reactions it was expected that mixtures of polycyclic and linear (possibly cross-linked) polysilanes will be formed. (Attempts to distill out pure compounds from our preparations were not successful. Less than 10% of the product was volatile at higher temperatures at 10^{-4} torr.). The ceramic yield obtained when the $[\text{CH}_3\text{SiH}]_{0.4}(\text{CH}_3\text{Si})_{0.6}]_n$ polymer was pyrolyzed (TGA to 1000°C) was 60%; a gray-black solid was obtained whose analysis indicated a composition $1.0 \text{ SiC} + 0.49 \text{ Si}$.

The reaction of methyldichlorosilane with sodium in a solvent system composed of six parts of hexane and one of THF gave a higher yield of product which was soluble in organic solvents. Such reactions give a colorless oil in 75 to over 80% yield which is soluble in many organic solvents. In various experiments the molecular weight (cryoscopic in benzene) averaged 520-740 and the constitution (by ^1H NMR) $[\text{CH}_3\text{SiH}]_{0.76}(\text{CH}_3\text{Si})_{0.24}]_n$ to $[\text{CH}_3\text{SiH}]_{0.9}(\text{CH}_3\text{Si})_{0.1}]_n$. The less cross-linked material (compared to the product obtained in THF alone) gave much lower yields of ceramic product on pyrolysis to 1000°C (TGA yields ranging from 12-27% in various runs). Again, the product was (by analysis) a mixture of SiC and elemental silicon, $1.0 \text{ SiC} + 0.42 \text{ Si}$ being a typical composition. These results are not especially promising, and it was obvious that further chemical modification of the $[\text{CH}_3\text{SiH}]_x(\text{CH}_3\text{Si})_y]_n$ products obtained in the $\text{CH}_3\text{SiHCl}_2/\text{Na}$ reactions was required.

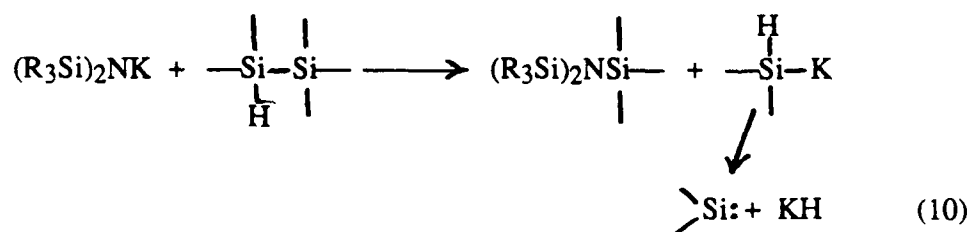
A number of approaches which we tried did not lead to success, but during the course of our studies we found that treatment of the $[\text{CH}_3\text{SiH}]_x(\text{CH}_3\text{Si})_y]_n$ products with alkali metal amides (catalytic quantities) serves to convert them to materials of higher molecular weight whose pyrolysis gives significantly higher ceramic yields. Thus, in one example, to 0.05 mol of liquid $[\text{CH}_3\text{SiH}]_{0.85}(\text{CH}_3\text{Si})_{0.15}]_n$ in THF was added, under nitrogen, a solution of about 1.25 mmol (2.5 mol% of $[(\text{CH}_3)_3\text{Si}]_2\text{NK}$ in THF. The resulting red solution was treated with methyl iodide. Subsequent nonhydrolytic workup gave a soluble white powder, molecular weight 1000, whose pyrolysis to 1000°C gave a ceramic yield of 63%.

The proton NMR spectrum of this product showed only broad resonances in the Si-H and Si-CH₃ regions. In the starting $[\text{CH}_3\text{SiH}]_x(\text{CH}_3\text{Si})_y]_n$ material, the observed proton NMR integration ratios, SiCH_3/SiH , ranged from 3.27-3.74. This ratio was quite different in the case of the product of the silylamide-catalyzed process, ranging from 8.8. to 14. Both Si-H and Si-Si bonds are reactive toward nucleophilic reagents. In the case of the alkali metal silylamides, extensive structural reorganization, involving

both Si-H and Si-Si bonds of the $[\text{CH}_3\text{SiH}_x(\text{CH}_3\text{Si})_y]_n$ polysilane, that results in further cross-linking, must have taken place. The following processes can be envisioned:



In each process, a new reactive nucleophile is generated: KH in equation 6, a silyl alkali metal function in reactions 7 and 8. These also could undergo nucleophilic attack on the $[\text{CH}_3\text{SiH}_x(\text{CH}_3\text{Si})_y]_n$ system and during these reactions some of the oligomeric species which comprise the starting material would be linked together, giving products of higher molecular weight. Other processes are possible as well, e.g., a silylene process as shown in equation 9. Thus not only anionic species but also neutral silylenes could be involved as intermediates. In any case, extensive loss of Si-H takes place during the catalyzed process: it is more than a simple redistribution reaction. Further studies relating



to the mechanism of the process must be carried out.

While these silylamide-catalyzed reactions provided a good way to solve the problem of the low ceramic yield in the pyrolysis of $[\text{CH}_3\text{SiH}_x(\text{CH}_3\text{Si})_y]_n$, the problem of the elemental composition of the ceramic product remained (i.e., the problem of Si/C ratios greater than one) since only catalytic quantities of the silylamide were used.

As noted above, KH-catalyzed polymerization of the $\text{CH}_3\text{SiHCl}_2$ ammonolysis product gives a "living" polymeric silylamide of type $[(\text{CH}_3\text{SiHNNH})_a(\text{CH}_3\text{SiN})_b(\text{CH}_3\text{SiHNK})_c]_n$. In a typical example, $a = 0.39$, $b = 0.57$, $c = 0.04$, so there is only a low concentration of potassium silylamide functions in the polymer. This polymeric silylamide reacts with electrophiles other than methyl iodide, e.g., with diverse chlorosilanes, and it has been isolated and analyzed. Since it is an alkali metal silylamide, we expected that it also would react with $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ polysilane-type materials. Not only would it be expected to convert the latter into material of higher molecular weight, but it also would be expected to improve the Si/C ratio (i.e., bring it closer to 1). As noted above, pyrolysis of $[(\text{CH}_3\text{SiHNNH})_a(\text{CH}_3\text{SiN})_b(\text{CH}_3\text{SiHNCH}_3)_c]_n$ gives a ceramic product in 80-85% yield containing (formally) Si_3N_4 , SiC and excess carbon. Thus, combinations of the two species in the appropriate stoichiometry, i.e., of $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ and $[(\text{CH}_3\text{SiHNNH})_a(\text{CH}_3\text{SiN})_b(\text{CH}_3\text{SiHNK})_c]_n$, and pyrolysis of the product (which we will call a "graft" polymer) after CH_3I quench could, in principle, lead to a ceramic product in which the excess Si obtained in pyrolysis of the former and the excess C obtained in the pyrolysis of the latter combine to give SiC. Accordingly, experiments were carried out in which the two polymer systems $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ and the "living" polymer-silyl amide, $[(\text{CH}_3\text{SiHNNH})_a(\text{CH}_3\text{SiN})_b(\text{CH}_3\text{SiHNK})_c]_n$ were mixed in THF solution in varying proportions (2.4:1 to 1:2 mole ratio) and allowed to react at room temperature for 1 h and at reflux for 1 h. (Such experiments were carried out with the $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ materials prepared in hexane/THF as well as with those prepared in THF alone.) After quenching with methyl iodide, nonhydrolytic workup gave a new polymer in nearly quantitative yield (based on weight of material charged). The molecular weight of these products was in the 1800-2500 range. Their pyrolysis under nitrogen gave ceramic products in 74-83% yield. Thus the reaction of the two polymer systems gives a new polymer in close to quantitative yield which seems to be an excellent new preceramic polymer in terms of ceramic yield. The formal compositions of the ceramic materials obtained cover the range $1 \text{ Si}_3\text{N}_4 + 3.3$ to $6.6 \text{ SiC} + 0.74$ to 0.85 C . Thus, as expected, they are rich in silicon carbide and the excess Si which is obtained in the pyrolysis of the $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ materials alone is not present, so that objective has been achieved. By proper adjustment of starting material ratios, we find that the excess carbon content can be minimized [23].

In an alternative method of synthesis of $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y][(\text{CH}_3\text{SiHNNH})_a(\text{CH}_3\text{SiN})_b]$ "combined" polymers, the polysilyl

amide was generated in situ in the presence of $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$. This, however, gave materials that were somewhat different. In one such experiment, a mixture of $[\text{CH}_3\text{SiH}(\text{NH})]_n$ cyclics (as obtained in the ammonolysis of $\text{CH}_3\text{SiHCl}_2$ in THF) and the $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ material ($x = 0.76$; $y = 0.26$) in THF was treated with a catalytic amount of KH. After the reaction mixture had been treated with methyl iodide, the usual workup gave an 89% yield of hexane-soluble white powder, molecular weight ~ 2750 . On pyrolysis, this material gave a 73% yield of a black ceramic.

The "combined" polymer prepared in this way ("in situ polymer") was in some ways different from the "combined" polymer prepared by the first method ("graft" polymer). Principal differences were observed in their proton NMR spectra and in the form of their TGA curves. This suggests that the two differently prepared polymers have different structures. It is likely that in the "in situ" preparation intermediates formed by the action of KH on the $[\text{CH}_3\text{SiH}(\text{NH})]_n$ cyclics are intercepted by reaction with the $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ also present before the $[(\text{CH}_3\text{SiH}(\text{NH}))_a(\text{CH}_3\text{SiH})_b(\text{CH}_3\text{SiHNK})_c]_n$ polymer (which is the starting reactant used in the "graft" procedure) has a chance to be formed to the extent of its usual molecular weight. Thus, less of the original $\text{CH}_3\text{SiH}(\text{NH})$ protons are lost and/or more of those of the $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ system are reacted.

The TGA curves of the "graft" polymer are different as well. Noteworthy in the former is a small weight loss between 100°C and 200°C , which begins at around 100°C . This initial small weight loss occurs only at higher temperature (beginning at $\sim 175^\circ\text{C}$) in the case of the "in situ" polymer. This difference in initial thermal stability could well have chemical consequences of importance with respect to ceramics and both kinds of polymers may be useful as preceramic materials.

Physical blends of $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ (solid polymer, THF preparation), and $[(\text{CH}_3\text{SiH}(\text{NH}))_a(\text{CH}_3\text{SiH})_b(\text{CH}_3\text{SiHNCH}_3)_c]_n$ were also examined. When about equimolar quantities of each were mixed and finely ground together, pyrolysis to 1000°C gave a 70% ceramic yield. It appears that a reaction between the two polymers already occurs at lower temperatures. When such mixtures were heated, either in the absence of a solvent at 100°C under nitrogen or in toluene solution at reflux, white powders were obtained which were insoluble in hexane, benzene, and THF. The ceramic yields were 67% and 75 %, respectively.

Further experiments showed that the "combined" polymers may be converted to black ceramic fibers. Pyrolysis of pressed bars of the "combined" polymer to 1000°C gave a black product of irregular shape (75-76% ceramic yield). In other experiments,

SiC powder was dispersed in toluene containing 20% by weight of the "combined" polymer. The solution was evaporated and the residue, a fine powder of SiC with the "combined" polymer binder, was pressed into bars and pyrolyzed to 1000°C. A ceramic bar (6% weight loss, slightly shrunk in size) was obtained.

The "living polymer" intermediate in our polysilazane synthesis is useful in "upgrading" other Si-H containing polymers for application as precursors for ceramic materials [24]. Another example of this application is provided by such "upgrading" of methylhydrogenpolysiloxane, $[\text{CH}_3\text{Si}(\text{H})\text{O}]_n$ to give a useful precursor for silicon oxynitride which is more resistant to high temperature oxidation than silicon nitride. Such a linear polymer, average molecular weight 2000-5000 (vendor data), on pyrolysis under argon to 1000°C, left a black ceramic residue of only 13%. In this study, experiments were carried out with a $[\text{CH}_3\text{Si}(\text{H})\text{O}]_m$ prepared using conditions under which the yield of the cyclic oligomers ($m = 4, 5, 6, \dots$) is maximized [25], as well as with the commercial $[\text{CH}_3\text{Si}(\text{H})\text{O}]_m$ polymer of higher molecular weight, with presumably high linear content.

In one approach, the polymeric postassium silylamide was prepared as described above (using the product of $\text{CH}_3\text{SiHCl}_2$ ammonolysis in THF) and to this "living" polymer solution were added slowly the $[\text{CH}_3\text{Si}(\text{H})\text{O}]_m$ oligomers (high cyclic content). An immediate reaction with some gas evolution occurred. The resulting clear solution was treated with CH_3I to react with any remaining silylamide units. Silylamide/siloxane weight ratios of 1:1 and 1:5 were used. In both cases the polymeric product was an organic-soluble white solid of moderate (1700 and 2400, respectively) average molecular weight. In both cases pyrolysis under nitrogen or argon gave high char yields (78% and 76%, respectively). Pyrolysis to 1000°C of a bulk sample of the 1:1 by weight polymer gave a black solid in 80% yield. Elemental analysis indicated a "composition": $1 \text{ SiC} + 0.84 \text{ Si}_3\text{N}_4 + 2.17 \text{ SiO}_2 + 2.0 \text{ C}$ (this is not meant to reflect the composition in terms of chemical species present). On the other hand, pyrolysis under gaseous ammonia gave a white ceramic solid in 78.5% yield. It is suggested that here also high temperature nucleophilic cleavage of Si-CH₃ bonds by NH₃ occurred and that the ceramic product is a silicon oxynitride. This was confirmed by analysis. The white solid contained less than 0.5% carbon.

In an alternate approach to this "graft" procedure the "in situ" procedure was used. A mixture (~1:1 by weight) of the $\text{CH}_3\text{SiHCl}_2$ ammonolysis (in THF) product, $[\text{CH}_3\text{SiH}_2\text{NH}]_m$, and the $\text{CH}_3\text{SiHCl}_2$ hydrolysis product, $[\text{CH}_3\text{Si}(\text{H})\text{O}]_n$, in THF, was added to a suspension of a catalytic amount of KH in THF. Hydrogen evolution was

observed and a clear solution resulted. After quenching with CH_3I , further work-up gave the new polymer, a soluble white powder, average molecular weight 1670. Pyrolysis to 1000°C (TGA) gave a black ceramic solid in 84% yield. Pyrolysis of a bulk sample under argon yielded a black ceramic (73%). Analysis indicated the "composition": $1 \text{ SiC} + 1.03 \text{ Si}_3\text{N}_4 + 1.8 \text{ SiO}_2 + 2.63 \text{ C}$.

In place of the (mostly) cyclic $[\text{CH}_3\text{SiHO}]_n$ oligomers, a commercial methylhydrogenpolysiloxane (Petrarch PS-122) of higher molecular weight, presumably mostly linear species, may serve as the siloxane component. When a 1:1 by weight ratio of the preformed polymeric silylamide and the $[\text{CH}_3\text{Si}(\text{H})\text{O}]_n$ polymer was used and the reaction mixture was quenched with CH_3I , the usual work-up produced a soluble white solid, molecular weight 1540. Pyrolysis of a bulk sample yielded a black solid (73% yield) whose analysis indicated a "composition": $1 \text{ SiC} + 1.5 \text{ Si}_3\text{N}_4 + 3.15 \text{ SiO}_2 + 3.6 \text{ C}$. Application of the "in situ" procedure [1:1 by weight ratio of $[\text{CH}_3\text{SiHNNH}]_n$ and $[\text{CH}_3\text{Si}(\text{H})\text{O}]_n$ gave a soluble white powder, average molecular weight 1740, pyrolysis yield 88% (black solid). The fact that the pyrolysis of these polymers under a stream of ammonia gives white solids, silicon oxynitrides which contain little if any, carbon, in high yield is of interest. The ceramics applications of the silicon oxynitride precursor systems have received further study by Yu and Ma of Universal Energy Systems [26].

The Nicalon polycarbosilane mentioned earlier, as obtained by thermal rearrangement of poly(dimethylsilylene), is a polymeric silicon hydride, with $[(\text{CH}_3)(\text{H})\text{SiCH}_2]$ as the main repeating unit. As such, it also might be expected to react with our $[(\text{CH}_3\text{SiHNNH})_a(\text{CH}_3\text{SiN})_b(\text{CH}_3\text{SiHNK})_c]_n$ living poly(silylamide). This was found to be the case [27]. The commercially available polycarbosilane (sold in the U.S. by Dow Corning Corporation; our sample, a white solid, molecular weight of 1210 and a ceramic yield of 58% on pyrolysis) was found to react with our poly(silylamide). A reaction carried out in THF solution, initially at room temperature, then at reflux, followed by treatment of the reaction mixture with methyl iodide, gave after appropriate workup a nearly quantitative yield of a white solid which was very soluble in common organic solvents including hexane, benzene, and THF. When the polycarbosilane-to-polysilylamide ratio was approximately one, pyrolysis of the product polymer gave a black ceramic solid in 84% yield which analysis showed to have a formal composition ($1 \text{ SiC} + 0.22 \text{ Si}_3\text{N}_4 + 0.7 \text{ C}$). When the polycarbosilane/polysilylamide ration was ~ 5 , the ceramic yield was lower (67%). In these experiments the cyclo- $[\text{CH}_3\text{SiHNNH}]_n$ starting materials used to synthesize the polysilylamide had been prepared by $\text{CH}_3\text{SiHCl}_2$ ammonolysis in diethyl ether. When this preparation was carried out in

THF, the final ceramic yields obtained by pyrolysis of the polycarbosilane/polysilylamide hybrid polymer were 88% (1:1 reactant ratio) and 64% (5:1 reactant ratio). The "in situ" procedure in which the $\text{CH}_3\text{SiHCl}_2$ ammonolysis product, cyclo- $[\text{CH}_3\text{SiHNH}]_n$, was treated with a catalytic quantity of KH in the presence of the polycarbosilane, followed by a CH_3I quench and the usual work-up, gave equally good results in terms of high final ceramic yields, whether the starting cyclo- $[\text{CH}_3\text{SiHNH}]_n$ was prepared in Et_2O or THF.

It is clear from these results that a new polymer is formed when the polycarbosilane and the polymeric silylamide are heated together in solution and then quenched with methyl iodide. Proton NMR spectroscopy brought further evidence of such a reaction. A physical mixture of the polycarbosilane and the polysilazane, $[(\text{CH}_3\text{SiHNH})_a(\text{CH}_3\text{SiN})_b(\text{CH}_3\text{SiHNCH}_3)_c]_n$, also was found to react when heated to 1000°C , giving good yields of ceramic product. That appreciable reaction had occurred by 200°C was shown in an experiment in which a 1:1 by weight mixture of the initially soluble polymers was converted by such thermal treatment to a white, foamy solid which no longer was soluble in organic solvents.

Finally, we mention another procedure for "upgrading" the $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ polysilanes. With their many Si-H bonds, they should be good candidates for crosslinking to a network polymer by means of hydrosilylation. Within that broad class of reactions, in terms of the polyolefinic compounds and the catalyst types that might be used [28], we found cyclo- $[(\text{CH}_3)(\text{CH}_2=\text{CH})\text{SiNH}]_3$ to be an especially good polyolefin which reacted very effectively with these polysilanes when the addition reaction was initiated by azobisisobutyronitrile, a radical catalyst [29]. When the crosslinking reaction was carried out using an $\text{SiH}/\text{SiCH}=\text{CH}_2$ ratio of 6 or larger, the products were white solids which all were soluble in organic solvents such as hexane, benzene, and THF. The yields were quantitative. The products are of fairly low molecular weight and, in some cases, quite satisfactory (68%, 77%) ceramic yields were obtained when these materials were pyrolyzed to 1000°C .

Pyrolysis of one of the products whose proton NMR spectrum and elemental analysis indicated a constitution $[(\text{CH}_3\text{SiH})_{0.73}(\text{CH}_3\text{Si})_{0.1}(\text{CH}_3)\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)\text{NH}]_{1.17}$, indicated a formal composition $1 \text{ SiC}/0.033 \text{ Si}_3\text{N}_4/0.04 \text{ C}$. Thus the stoichiometry and reaction conditions in this experiment gave a high yield of a ceramic product which was silicon carbide contaminated with only minor amounts of silicon nitride and free carbon. When such a pyrolysis was effected to

1500°C, the ceramic product was at least partly crystalline. X-ray diffraction showed only lines due to β -SiC.

EPILOGUE

The design of useful, (i.e., potentially commercializable) organosilicon preceramic polymers presents an interesting challenge to the synthetic chemist. We have attempted, using examples from some of our research, to convey some of the chemical considerations which we feel are important if such a synthesis is to be successful. Our initial experiment in this area, the reaction of ammonia with dichlorosilane, was carried out by Dr. Christian Prud'homme in April 1981. This project then was taken over by a graduate student, Gary H. Wiseman, who during the course of his Ph.D. research developed the dehydrocyclodimerization route to useful preceramic polymers and widened our horizons into the fascinating area of ceramics. It was another graduate student, Dr. Timothy G. Wood, who studied the action of sodium on $\text{CH}_3\text{SiHCl}_2$ and carried out the first "graft" synthesis of the polysilazane/polysilane hydrid polymer, as the last experiment of his thesis work. Further contributions to the development of this area were made by Joanne M. Schwark, a graduate student, and by several postdoctoral coworkers: Charles A. Poutasse, Yun Chi, Yoshio Inoguchi, Tom S. Targos and especially Yuan-Fu Yu.

Research in the preceramic polymer area, if it is to come to fruition, must be an interdisciplinary endeavor. After the chemistry has been developed, there are important ceramics issues to be addressed. "Good" chemistry does not guarantee "good" ceramics! However, there is the possibility that the chemistry still can be modified to give "good" ceramics. Either the chemist must learn a good bit about ceramics characterization and processing or, better, he must work closely together with the ceramist. We have been most fortunate to find very helpful colleagues in the ceramics area: Mr. Roy W. Rice, when he was still at the Naval Research Laboratory, and his coworkers, and Professor H. Kent Bowen and Dr. John S Haggerty and their colleagues at the Ceramics Processing Research Laboratory at M.I.T.

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